1 Introduction

1.1 Phosphinoamide

Phosphinoamides and their derivatives are a series of compounds featuring a phosphorus(III)-nitrogen(III) bond. Compounds containing a P-N single bond (Cl_2P-NR_2, $Cl_2P-N(H)R$, and $RP(NR'_2)_2$) have been first reported by Michaelis.[1,2] Later on, this series of compounds was expanded with some further examples including $(CF_3)_2P-N(H)Me$ and R_2P-NR_2 (R = Me, Et, Ph).[3-5] With few exceptions, P-N bond can be formed by three general pathways (Scheme 1.1.1): 1, by the aminolysis reaction between a halogenophosphine and a primary or secondary amine, through the elimination of HCl with an organic base (eqn. **1**); 2, by salt metathesis (salt elimination) between a chlorophosphine and an alkali metal amide (eqn. **2**); 3, by the elimination of Me_3SiCl from the reaction between a chlorophosphine and an aminosilane (eqn. **3**).[6-11] Instead of alkyl groups, aryl groups are more suitable for the synthesis of phosphinoamides. Indeed, an aryl group on the phosphorus atom can shorten the distance of the P-N bond by decreasing the electron density on the phosphorus.[12-14] In addition, quantum chemical calculation revealed that σ-acceptor substituents (*e.g.* fluorine) on the phosphorus atom could further strengthen the P-N bond. On the contrary, electron-withdrawing substituents on the nitrogen atom weaken the bond.[15]

$$R_2NH \quad + \quad ClPR'_2 \xrightarrow{\text{Base}} R_2N\text{-}PR'_2 \qquad (\mathbf{1})$$

$$R_2NLi \quad + \quad ClPR'_2 \xrightarrow{\text{- LiCl}} R_2N\text{-}PR'_2 \qquad (\mathbf{2})$$

$$R_2NSiMe_3 \quad + \quad ClPR'_2 \xrightarrow{\text{- ClSiMe}_3} R_2N\text{-}PR'_2 \qquad (\mathbf{3})$$

Scheme 1.1.1 General pathways to form a P-N bond.

The phosphinoamide chemistry has attracted a considerable attention owing to the structural diversity of the associated complexes.[16-21] To further understand the properties of the P-N bond, Ashby synthesized the compound $[(Ph_2P-NPh)Li(Et_2O)]_2$ (Figure 1.1.1) through the deprotonation reaction of the corresponding aminophosphine with ^{n}BuLi.[22] X-ray diffraction analyses indicated the presence of Li-P bonds (2.684(3) and 3.004(4) Å). In addition, the P-N bond length (1.672(2) Å) was relatively smaller than that of a single bond (mean value of 1.70

Å), which indicates that the P-N bond distance in phosphinoamides falls between single- and double-bond distances.

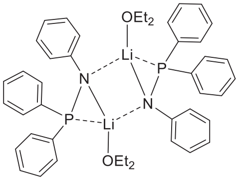


Figure 1.1.1 Molecular structure of $[(Ph_2P\text{-}NPh)Li(OEt_2)]_2$.

Quantum chemical calculations revealed that the $[Ph_2PNPh]^-$ anion exhibits two resonance forms: phosphinoamide (negative charge located on N) and iminophosphide (negative charge located on P) (Figure 1.1.2). A possible explanation is the stabilization of the charge α to the phosphorous by negative hyperconjugation.[23,24] Further theoretical studies indicate that in most case the negative charge is placed on the more electronegative nitrogen atom.

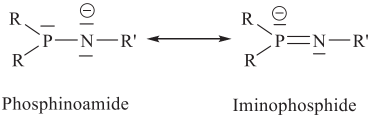


Figure 1.1.2 Resonance forms of phosphinoamide and iminophosphide.

Two ground-state conformations, *cis* and *trans*, can be proved in the molecular structure of phosphinoamide derivatives (Figure 1.1.3). Theoretical calculations revealed that the interconversion barrier between the *cis* and *trans* isomers could be influenced by the nature of substituents. Apart from this, negative hyperconjugation could significantly affect the conformation of phosphinoamides. Specifically, phosphinoamides prefer to adopt a *cis* conformation in spite of the unfavorable steric.[25]

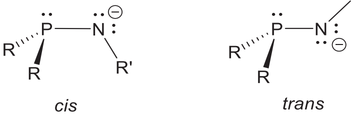
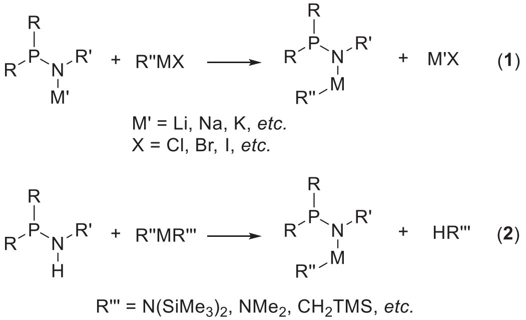


Figure 1.1.3 Ground-state conformations of phosphinoamide.

1.2 Metal complexes of phosphinoamide

Given the presence of lone pairs on both the nitrogen and phosphorus atoms, phosphinoamides and their derivatives have been widely used as ligands to establish various metal complexes.[17,26-33] In particular, the "hard" nitrogen atom could stabilize metals in high oxidation states, while the "softer" phosphorus atom is a good candidate to coordinate to metals in medium and low oxidation states. The first metal complexes of phosphinoamides, $[(Ph_2P\text{-}NEt_2)CuI]_4$ and $[(Ph_2P\text{-}NEt_2)HgI_2]$, were established in 1962.[3] Metal complexes of phosphinoamide can be synthesized following two typical reaction pathways (Scheme 1.2.1): 1, through a salt metathesis reaction (**1**) between an alkali metal salt of phosphinoamide and a metal halide; 2, through an intermolecular deprotonation reaction (**2**) between a metal complex bearing a basic ligand and an aminophosphine.



M' = Li, Na, K, *etc.*
X = Cl, Br, I, *etc.*

R''' = $N(SiMe_3)_2$, NMe_2, CH_2TMS, *etc.*

Scheme 1.2.1 Typical reaction pathways to synthesize phosphinoamide metal complexes.

Possessing both a hard donor atom (nitrogen) and a soft donor atom (phosphorus), phosphinoamides can exhibit various coordination modes with metal centers, acting as either monodentate, bridging or chelating ligands (Figure 1.2.1). As a monodentate ligand (**a**), the nitrogen atom directly connects to the metal center, while the lone pair on the phosphorus atom is free. As a bridging ligand (**b**), the nitrogen and phosphorus atoms connect to two different metal centers. As a chelating ligand (**c**), both the nitrogen and phosphorus atoms coordinate to one metal atom, giving a three-membered ring.

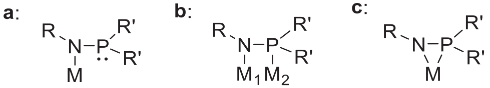


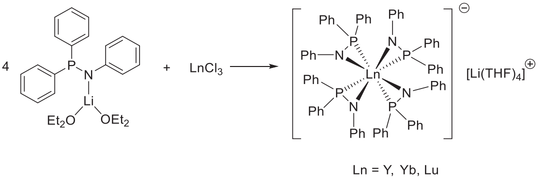
Figure 1.2.1 Coordination modes of phosphinoamide ligands.

Over the past two decades, various phosphinoamides and their metal complexes have been established and displayed promising applications. Phosphinoamide metal complexes have proved to be good catalysts in polymerization, hydroamination, hydroboration *etc.*.[34-42] Transition metal and lanthanide complexes have especially shown interesting magnetic properties.[43-45] In addition, the biological activities could be confirmed for some phosphinoamide compounds.[46-48]

1.2.1 Lanthanide complexes of phosphinoamide

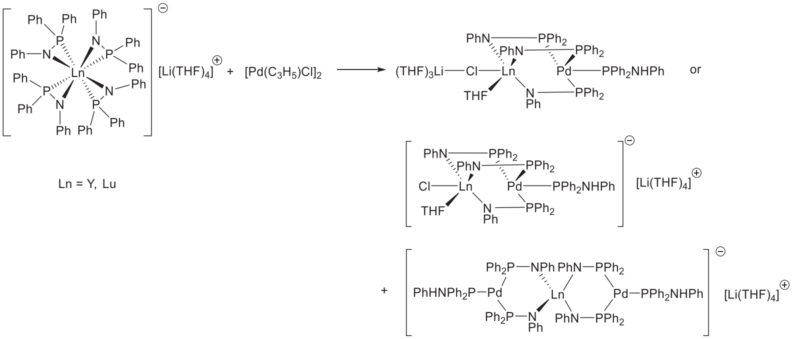
Lanthanides, abbreviated to Ln, are the series of chemical elements from lanthanum to lutetium (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). Owing to the existence of the 4f electron shell, lanthanides correspond to f-block elements. One of their most interesting features lies in the lanthanide contraction corresponding to a steady decrease in the ionic radii from lanthanum to lutetium. Owing to the presence of the 4f electron shell and the lanthanide contraction, lanthanide elements and their derivatives manifest specific spectroscopic and magnetic properties compared to transition metals and main group elements.

In 1999, three homoleptic lanthanide complexes of phosphinoamides, consisting only of three-membered metallacycles (η^2-coordinated chelating ligands), were established by our group[49], *via* a salt metathesis reaction, between lithium phosphinoamide and anhydrous $LnCl_3$ (Ln = Y, Yb, Lu) (Scheme 1.2.1.1). As soft Lewis bases, the four phosphorus atoms in the complexes formed very weak interactions with the lanthanide atom (hard acid), with bond distances varying from 2.885(2) to 3.040(3) Å.



Scheme 1.2.1.1 Synthesis of homoleptic phosphinoamide lanthanide complexes.

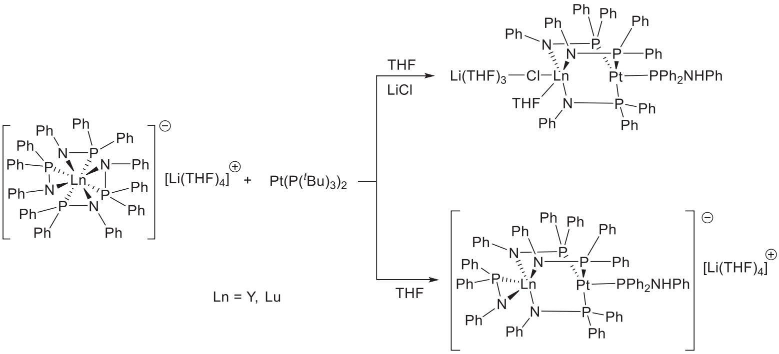
Furthermore, the palladium allyl precursor ($[Pd(C_3H_5)Cl]_2$) was utilized to establish Ln-Pd (Ln = Y, Lu) heterobimetallic complexes (Scheme 1.2.1.2).[50] The isolated heterobimetallic Ln(III)-Pd(0) complexes revealed differences compared to their corresponding Zr-Pd complexes. Indeed, the unexpected reduction of $[Pd(C_3H_5)Cl]_2$ and the formation of one neutral ligand, Ph_2P-N(H)Ph, were observed, leading to the formation of unanticipated bimetallic Ln(III)-Pd(0) complexes and trimetallic Pd(0)-Ln(III)-Pd(0) complexes. It was suggested that the $Ph_2PN(H)Ph$ ligand comes from the decomposition of $[(Ph_2PNPh)_4Ln][Li(THF)_4]$. X-ray diffraction analyses and quantum chemical calculations illustrated the presence of the Ln-Pd interactions with bond lengths ranging from 2.9031(11) Å to 3.1860(12) Å.



Scheme 1.2.1.2 Synthesis of phosphinoamide-supported Ln-Pd complexes.

Inspired by the above Ln(III)-Pd(0) complexes, some phosphinoamide-supported Ln(III)-Pt(0) complexes have also been reported by our group, through the reaction of $[(Ph_2PNPh)_4Ln][Li(THF)_4]$ (Ln = Y, Lu) with $[Pt(^tBu_3P)_2]$ (Scheme 1.2.1.3).[51] The platinum atom could displace the phosphine donors, resulting in the cleavage of the three Ln-P bonds and the formation of Ln-Pt interactions (Y-Pt: 3.0063(8) Å and Lu-Pt: 2.9523(9) Å). In addition, the presence of LiCl could influence the outcome of this reaction. Specifically, in the absence of

LiCl, one phosphinoamide anion $[PPh_2NPh]^-$ chelates the lanthanide atom forming a three-membered metallacycle, while, in the presence of LiCl, one $[LiCl(THF)_3]$ moiety is coordinated to the lanthanide ion via a bridging chloride atom.

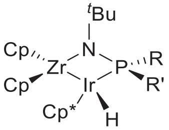


Scheme 1.2.1.3 Synthesis of phosphinoamide-supported Ln(III)-Pt(0) heterobimetallic complexes.

1.2.2 Group 4 metal complexes of phosphinoamide

Group 4 is the group of elements containing titanium (Ti), zirconium (Zr), hafnium (Hf) and rutherfordium (Rf), with a $(n-1)d^2ns^2$ electron configuration, favoring the +4 oxidation state. For titanium, the oxidation states of +2 and + 3 have been confirmed. Due to the lanthanide contraction, zirconium and hafnium have a very close atomic radius and thus manifest very similar chemical reactivity.

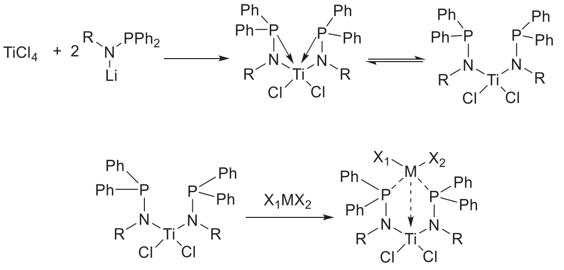
After the report of the first heterobimetallic phosphinoamide group 4 complexes in 1993 (Figure 1.2.2.1)[52], large amounts of phosphinoamide group 4 complexes have been established in the past decades.[53-63]



R = ethyl, H
R' = ethyl, cyclohexyl

Figure 1.2.2.1 Molecular structure of the first group 4 phosphinoamide complexes.

Reaction of $TiCl_4$ with 2 equiv. of lithium phosphinoamide resulted in the formation of their corresponding bis-substituted titanium complexes (Scheme 1.2.2.1).[64] X-ray diffraction analyses indicated the existence of Ti-P interactions with distances ranging from 2.4223(9) to 2.476(2) Å. To investigate the possibility to form Ti-Pt interactions, different platinum precursors were utilized to react with the bis(phosphinoamide)titanium complex. Both X-ray diffraction analyses and variable-temperature NMR experiments confirmed the existence and fluxionality of the Pt-Ti dative bonds (bond distances of 2.6860(11) to 2.8358(8) Å).

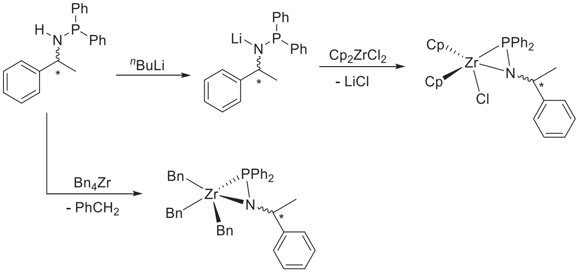


R = ^{t}Bu, ^{i}Pr

X_1MX_2 precursor	Heterobimetallic complexes
$(COD)PtCl_2$	M = Pt, $X_1 = X_2 = Cl$
(COD)PtMeCl	M = Pt, $X_1 = Cl$, $X_2 = Me$
(COD)Pt(p-Tol)Cl	M = Pt, $X_1 = Cl$, $X_2 = p$-Tol
$Me_2Pt(\mu SMe_2)$	M = Pt, $X_1 = X_2 = Me$

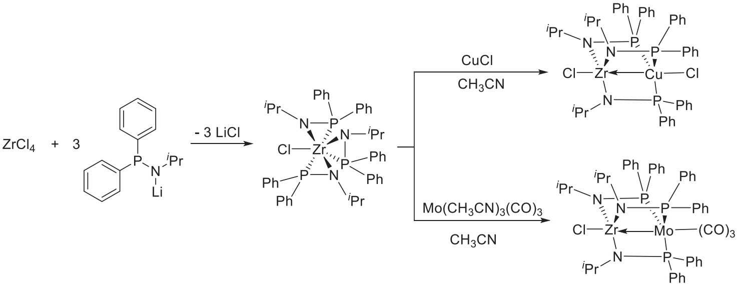
Scheme 1.2.2.1 Synthesis of phosphinoamide-supported Ti/Pt complexes.

In 2005, chiral phosphinoamide ligands were introduced into the group 4 coordination chemistry by our group (Scheme 1.2.2.2).[65] Salt metathesis reactions of the chiral lithium phosphinoamides with Cp_2ZrCl_2 led to the formation of the corresponding mono-substituted zirconium complexes. X-ray diffraction analyses revealed that the phosphorus atom is bonded to the zirconium atom with bond distances of 2.652(1) Å (*S*) and 2.650(2) Å (*R*). Alternatively, the enantiomerically pure mono-substituted complex was synthesized from the neutral amine and [$(PhCH_2)_4Zr$], *via* an intermolecular deprotonation reaction. It was suggested that the nature of the substituents on the zirconium atom could influence the Zr-N bond distance (2.1927(14) Å (R = Cp) *vs* 2.096(2) Å (R = Bn)).



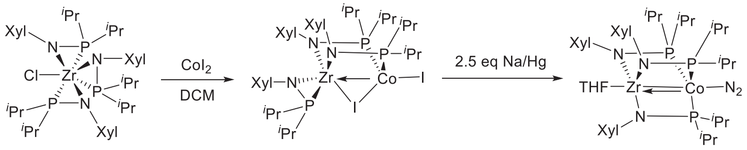
Scheme 1.2.2.2 Synthesis of chiral phosphinoamide zirconium complexes.

Nagashima reported the synthesis of tris(phosphinoamide)zirconium complexes through the reaction of $ZrCl_4$ with 3 equiv. of lithium phosphinoamides (Scheme 1.2.2.3).[66] X-ray diffraction studies indicated the existence of three P-Zr interactions with bond distances varying from 2.608(2) to 2.6656(9) Å. After further reaction with CuCl and [$Mo(CO)_3(CH_3CN)_3$] in CH_3CN, the corresponding phosphinoamide-supported heterobimetallic Zr-TM complexes were established with Zr-TM distances of 2.6854(6) Å (Zr-Cu) and 2.9741(5) Å (Zr-Mo).



Scheme 1.2.2.3 Synthesis of the tris(phosphinoamide)zirconium complex and its heterobimetallic Zr/Cu and Zr/Mo complexes.

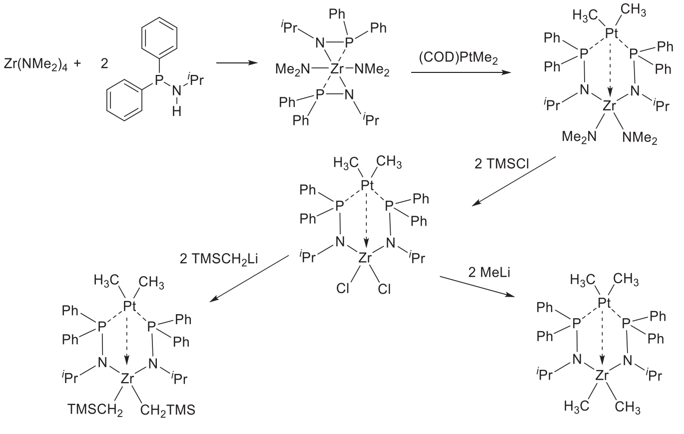
In 2014, Zr/Co heterobimetallic complexes bridged by phosphinoamides were crystallographically authenticated by Thomas.[67] CoI_2 was treated with [$({}^iPr_2PNXyl)_3ZrCl$] to generate the desired Zr/Co complex. After further reduction with 2.5 equiv. of Na/Hg, the expected phosphinoamide-supported heterobimetallic complex was obtained with a Zr-Co bond distance of 2.3778(5) Å (Scheme 1.2.2.4).



Scheme 1.2.2.4 Synthesis of phosphinoamide-supported Zr/Co complex.

To investigate the influence of the electron properties of the substituents on the metal-metal interaction, several zirconium/platinum complexes with substituents of varying electron-releasing ability was synthesized and structurally characterized (Scheme 1.2.2.5).[68] It was suggested that electron-withdrawing ligands on the zirconium atom could decrease the Pt-Zr distance. Instead, electron rich ligands could increase this separation (2.7761(5) Å (R = Cl) *vs* 3.2343(3) Å (R = NMe_2)).

Thomas and coworkers suggested that the metal-to-metal interaction could be regulated in phosphinoamide-supported early/late heterobimetallic complexes.[37,69,70] However, some obstacles in this field should not be ignored, such as the deficiency of suitable ligands.

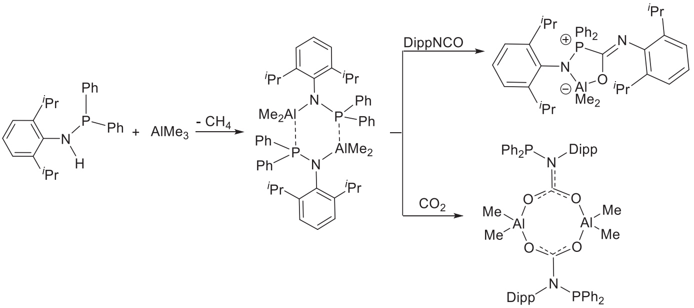


Scheme 1.2.2.5 Synthesis of phosphinoamide-supported Zr/Pt complexes.

1.2.3 Group 13 metal complexes of phosphinoamide

Group 13 contains boron (B), aluminum (Al), gallium (Ga), indium (In) and thallium (Tl). Since the possession of three electrons in the valence shell with the electron configuration of ns^2np^1, they prefer the oxidation state +3 except for the heaviest element thallium (+1 oxidation state favored).

Only one example of a group 13 metal phosphinoamide complex has been reported. In 2017, Harder synthesized the corresponding aluminum α-phosphinoamide complex from the reaction of $Ph_2PN(H)Dipp$ with $AlMe_3$ *via* an aminolysis reaction (Scheme 1.2.3.1).[71] This complex is dimeric bridged by two weak Al-P interactions (3.0396(12) Å). In addition, its frustrated Lewis pair reactivity towards isocyanates and CO_2 were investigated, on account of the mismatch between the aluminum (hard Lewis acid) and phosphorus atom (soft Lewis base).



Scheme 1.2.3.1 Frustrated Lewis pair reactivity of an aluminum phosphinoamide complex.

No gallium or indium complex of phosphinoamides has ever been reported. It should be mentioned that treatment of the lithium salt of bis(phosphinimino)amines with the appropriate metal halides MX_3 (M = Al, Ga, In, X = Cl, Br), *via* salt metathesis, resulted in the desired dihalo complexes of bis(phosphinimino)amine with formation of a six-membered N_3P_2M ring.[72]

1.2.4 Group 14 metal complexes of phosphinoamide

Group 14 is composed of carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). These elements possess the valence electron configuration ns^2np^2. Carbon and silicon prefer to adopt